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DETERMINATION OF SMALL AMOUNTS OF MOLYBDENUM IN TUNGSTEN

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The increasing use of tungsten and molybdenum in commercial alloys has demonstrated the need of better methods of analytical separation than those now in use. The difficulty of this separation is well known. When the metals occur together in not greatly different proportions existing methods may for most purposes be regarded as adequate. It is when one occurs in the presence of the other as a mere trace, but for many purposes an important amount, of impurity, that the difficulties become significant. This paper deals with one phase of the problem; that of the determination of molybdenum as an impurity in tungsten.

Descriptions of a number of methods for this purpose have been published:[1,2,3,4,5,6] The method first suggested by Siewert,[7] and later developed qualitatively by Malowan[8] and Koppel,[9] which seems to be more delicate than any previously described, depends upon the conversion of molybdenum to molybdenum xanthate and its separation from tungsten by dissolving the molybdenum compound in some non-miscible organic solvent. Siewert, using the method qualitatively only, noted that the molybdenum compound was slightly unstable in the presence of phosphoric, formic and acetic acids and too unstable to be of any use in the presence of tartaric and oxalic acids.

Malowan made use of the method both qualitatively and quantitatively in working out a colorimetric method in 30% acetic acid. He states that tungsten, uranium, vanadium and titanium gave no reaction with potassium xanthate and that he was able to separate molybdenum from iron. He gives a list of results obtained by the colorimetric analysis of molybdenum steels. A complete discussion of the qualitative value of the method is given by J. Koppel. He was able to detect molybdenum in the presence of other colored compounds by the strong color of molybdenum xanthate.

The method herein described for the separation of molybdenum from tungsten is based on the formation of the above-mentioned molybdenum xanthate, which is soluble in ordinary organic solvents. When separated by extraction the molybdenum may be precipitated as sulfide and ignited to oxide or precipitated as lead molybdate.

As described below, the separation of molybdenum is accomplished in a

[1] Rose, Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., vol. 2, p. 296, **1911.**

[2] Pechard. Ref. 1, p. 295.

[3] Smith and Reugenberg, THIS JOURNAL, **22,** 772 (1900).

[4] Ibbotson and Brearley, *Chem. News,* **81,** 15 (1900).

[5] Mdivani, *Bull. soc. chim.,* [4] **9,** 122 (1911).

[6] Marbaker, THIS JOURNAL, **37,** 86 (1915).

[7] Siewert, *Z. ges. Naturw.,* **4,** 23 (1864).

[8] Malowan, *Z. anorg. Chem.,* **108,** 73 (1919).

[9] Koppel, *Chem. Ztg.,* **43,** 777 (1919).

solution acid with a mineral acid. The precipitation of the tungsten on acidification is prevented by a slow addition of the acid, forming thereby metatungstic acid which remains clear if not heated. On addition of the xanthate the tungstate is reduced, giving a clear blue solution. Chloroform in this mixture causes a slight turbidity which, however, is of no consequence.

In a volume of 30 cc., 0.01 mg. of molybdenum can be detected by its red color; in 50 cc. it is pale pink. Small amounts of molybdenum give a clear red to plum colored solution, larger amounts give turbidity, and a still greater quantity will separate as a dark oil. It appears to be necessary to have a mineral acid present for the formation of the molybdenum compound; all of the organic acids tried bleached the color. Heating the chloroform extract causes decomposition of the molybdenum compound and a separation of the molybdenum sulfide and oxide.

The method is not recommended for amounts of molybdenum exceeding 5 mg. since the extract becomes bulky. More than 1 g. of tungsten makes the separation tedious, owing to the repeated extractions required.

Based on these considerations, the procedure is as follows. The molybdenum solution is neutralized with 0.2 *N* sodium hydroxide solution; solid potassium xanthate is added, about 0.5 g. at a time, then several drops of 1–3 sulfuric acid. In order to form the soluble metatungstate, the acid is added dropwise, with agitation of the solution after the addition of each drop until the curdy precipitate of tungstic acid has redissolved. A certain state of acidification is reached after which no amount of acid will effect a precipitation of tungsten while cold. On addition of the acid there appears a white turbidity due to formation of molybdenum xanthate, which turns red in a few seconds. The red molybdenum compound is extracted with chloroform and the extract drawn off from the bottom of the funnel into a second separatory funnel, where the extract is washed with water several times to remove any soluble salts and, in the case of a tungsten separation, to free it from the pentoxide (W_2O_5). The molybdenum extract is evaporated to dryness, and the residue dissolved in nitric acid, after which the molybdenum may be determined by any well-known method.

Experimental Part

Purified sodium tungstate was used for all of the synthetic mixtures employed in developing the method. Purified oxide was used for the standard molybdenum solution. Determination of the molybdenum in this solution when precipitated as sulfide, and ignited to oxide gave the following results: taken, 3.0, 6.0, 6.0 mg.; found, 2.9, 6.2, 6.0 mg.

C. P. Chloroform was used for the extractions. The potassium xanthate was prepared according to the description given in Richter's "Organic Chemistry."[10]

[10] Richter, "Organic Chemistry," P. Blakiston's Son and Co., **1916**, vol. 1, p. 433.

Molybdenum trioxide was dissolved in ammonia, and acidified with a few drops of sulfuric acid. The solution was made up to a definite volume so that 1 cc. contained 0.1 mg. of molybdenum. Aliquot portions of the standard solution were taken for the experiments. The molybdenum solution, in a 200cc. separatory funnel, was then diluted to 150 cc., 0.5 g. of solid potassium xanthate added, the solution acidified with a few drops of 1–3 sulfuric acid and shaken thoroughly. About 10 cc. of chloroform was added and the flask stoppered and shaken for several minutes. The chloroform layer separating at the bottom was run into a second funnel for washing. This addition of potassium xanthate, acid and chloroform was continued until the chloroform layer was colorless.

The molybdenum xanthate solution was washed by shaking several times with distilled water, and then run into a 150cc. beaker and evaporated to dryness. The molybdenum compound was then heated and thus converted to oxide and sulfide. It was then dissolved in nitric acid, evaporated with sulfuric acid, and precipitated as molybdenum sulfide by passing hydrogen sulfide into the hot molybdenum solution made alkaline with sodium hydroxide. The solution was then slowly acidified with dil. sulfuric acid and the sulfide precipitate was filtered, washed with hot water and carefully ignited to the trioxide.

The following results were obtained.

Mo present	Mo found	Mo present	Mo found
Mg.	Mg.	Mg.	Mg.
1.0	1.5	3.0	3.6
2.0	2.3	3.0	2.9
1.5	1.5	6.0	6.2
2.0	2.0		

Sodium tungstate equivalent to 700 mg. of tungsten was added and the separation carried out as previously described with the following results.

Mo present	Mo found	Mo present	Mo found
Mg.	Mg.	Mg.	Mg.
1.0	1.1	1.5	1.6
2.0	2.0	2.0	1.7
1.5	2.0	3.1	2.7

The method was next applied to stock samples of unknown composition. One-g. samples of these alloys were dissolved in nitric and hydrofluoric acids and evaporated with sulfuric acid. The yellow oxides were dissolved in sodium hydroxide solution and transferred to a separatory funnel. The solution was then treated as previously described. The extractions were combined and evaporated, the molybdenum being precipitated as sulfide and ignited to oxide. The results are indicated in the following table.

Sample no.	Mo found	Mo	Sample no.	Mo found	Mo
	Mg.	%		Mg.	%
121	3.28	0.28	122	2.14	0.40
	3.21	0.27		2.20	0.41
121 A	2.41	0.217	122 D	2.20	0.38
	3.75	0.224		2.47	0.44

Tungsten metal supposed to be free from molybdenum was found by this method to contain 0.078 and 0.074%.

As acetic acid can be used freely for acidification of tungstate solution without risk of precipitating tungstic acid, an attempt was made to devise a procedure which would avoid the observed instability of the molybdenum xanthate in the presence of this acid.

It was found that the acetic acid must be added after the xanthate and the extraction made as rapidly as possible, for when added before the xanthate, the results obtained are very low, showing a decomposition of the molybdenum compound. Molybdenum xanthate in the absence of tungstate may be extracted without loss, but tungsten seems to accelerate decomposition of the molybdenum compound. Under the most favorable conditions the average error was —0.54 mg. in 3.4 mg. of molybdenum (when tungsten was present) and the quantity of acetic acid seemed to be without effect.

Attempts to separate molybdenum from iron, nickel, vanadium, and uranium were unsuccessful. Contrary to Malowan's statement, these elements form with potassium xanthate colored compounds under the same conditions as molybdenum and these compounds are also soluble in chloroform. Traces of any of the above elements as impurities can, however, be removed by known procedures during the final separation of molybdenum.

A colorimetric method has not been tried, but does not seem promising, owing to the volatility of the organic solvent and the instability of the molybdenum compound.

Summary

A method has been described for the separation of small amounts of molybdenum from tungsten, consisting in the extraction of molybdenum xanthate by means of chloroform from a solution slightly acid with sulfuric acid.

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